VI

CHEMISTRY IN THE INDUSTRIES

CHEMICAL INDUSTRY, in the United States, grew directly in answer to needs violently made evident by World War I. Before the War, American-made dyes were not even listed in the official census reports. Our farmers had to buy German potash and Chilean nitrate. Our physicians looked to Europe for important drugs and optical glass. America-bound ships, heavy with goods and raw materials, testified to our dependency upon foreign countries. At that time our homes differed little from those of our grandfathers; we used the same textiles for our clothes and the same finishes on our horseless carriages. All steel rusted. The best rubber tires were worn out after about three thousand miles of highly uncertain road service. During the war there was the terrific driving power of necessity. There was the insistent urge to do bigger and better things, faster and faster. Ideas were translated into practice. Better methods were developed. New machines and products appeared.

After the War every branch of American industry seemed to possess a consciousness of the enormous power of science and the significance of its application to industry. Here was a challenge to improve upon the old methods and customs, a time to branch out into absolutely new territory. Here was the time to make use of potential ideas and abundant raw materials. And so there came to the chemical laboratories, textiles, steel, transportation, food and other industries.

"It is science, not governments nor wars of conquest, that

opens to us new horizons." These words, spoken by the late Andrew W. Mellon, will bear repeating in these troubled times. This American industrialist realized that "improvement in the standard of living can come about only by reason of new discoveries and inventions."

The new nation, which appeared on this continent following 1918, would have seemed a fantastic wonderland in 1914 had anyone then had the imagination to foresee it. The automobile came of age; aviation was established as an industry; and the wireless of war became radio. When, on December 7, 1941, we found ourselves again at war on a global scale, we were living on a plane that bore little resemblance to the pre-war period of a quarter century earlier. Our clothes, our food, our homes, and our industry were all different. Furniture and hosiery alike were being made from coal, water, and air; dresses from wood, farm fertilizers from the atmosphere, and camphor from pine stumps.

This is a war of many metals, for we live in the age of alloys. An American bomber, fourteen tons of fiber and metal, waddles to the head of the long runway, poises for a moment, there is a thunderous roar, and she takes off. Her aluminum skin is dark with war paint, a camouflaging coat of dull black, dirt brown, and forest green. This metal marvel is answering the terrific pull of 4,800 mechanical horses. And yet each of these horses weighs barely over a pound. This wonder is achieved by modern chemical and mechanical genius working with new lightweight metals and new high-strength alloys. Here are aluminum, magnesium, and beryllium along with tungsten, vanadium, and molybdenum. Here are plastics, fabrics, and alloys, each efficiently doing its important part. The metals and alloys are fibers of strength in a great industrial nation. In this war of many metals the lack of a single one may be a blow worse than the loss of a battle.

Two of the most useful of all the metals exist on the earth in fantastic abundance—aluminum in the clay underfoot and magnesium in sea water. But so complicated is the job of extraction that we have known these metals in quantity for only a generation. Today, in airplanes and bombs of war, these lightweights shake the world. Aluminum, about one-third as heavy as iron, and magnesium, less than one-fourth of iron's weight, are chiefly responsible for the wonderfully low ratio of weight to power in the airplane engines.

Aluminum owes its origin, in its pure form, to the persistence and genius of a young American named Charles Martin Hall who, in 1886, discovered that when aluminum, purified from bauxite, was dissolved in a molten bath of cryolite, aluminum could be obtained by the electrolysis of this fused mass. Strategically our chief concern was the supply of cryolite and the production capacity of alumina plants. Fortunately, for this program, President Wilson was farsighted in pushing construction of enormous water power projects along the Tennessee and Columbia rivers. The aluminum industry is now using artificial cryolite. Aluminum can be extracted from alunite and this is now being done by a newly developed process.

Some twenty years ago a German scientist discovered that if aluminum were mixed with about four per cent of copper, one-half of a per cent each of magnesium and manganese, and if the resulting alloy were heated, quenched, and then allowed to age for several days—this light and relatively soft, weak metal increased its strength fourfold. This alloy is "Duralumin." New alloys, typified by 25S and 24S, have been developed which combine easy forgeability with good strength. Many of the alloys are quite vulnerable to corrosion. Pure aluminum, on the other hand, is highly resistant to corrosion since it immediately acquires a virtually invis-

ible coating of oxide which generally protects it from further attack. To meet this problem there has been developed a method of producing "Alclad" sheet with the strong alloy wearing a thin skin of protective pure aluminum. Wings of planes are made of this protected metal.

Aluminum, in this war, finds itself being used as an avenging agent of destruction. Powdered aluminum, plus iron oxide, forms the dreaded thermite used in incendiary bombs. In some bombs, the thermite merely serves to ignite magnesium which burns with an intense heat and a vivid white light.

In 1918 less than 150 million pounds of aluminum were produced. Direct war needs of aluminum in 1942 totaled around one billion pounds and the demand in 1943 will rise to two billion pounds.

On the wall of General Somervell's office hangs this motto: "We do the impossible immediately; the miraculous takes a little longer." This is just about what is taking place today. Laboratories are actively engaged in overcoming the difficulties encountered in the various industries and in controlling the production of practically every essential war material.

The story of the production of magnesium is extremely interesting. Its extensive commercial production is a triumph in the field of chemistry. One hundred years ago a scientist could have accurately stated that in 1943, man would be flying in the air like a bird; and that much of the metal out of which his machine was built had come from sea water and clay. It would be interesting to know how such a statement would have been received. For the first time in the history of the world a structural metal is being obtained from the sea. The magnesium is precipitated from the sea water as the hydroxide; the hydroxide is neutralized with hydro-

chloric acid; the chloride is dried, and then fused and electrolyzed in cells where the metal rises to the top and is skimmed off. The lightness of magnesium is amazing. A magnesium alloy girder, which one man can handle with ease, will support the weight of a heavy automobile.

Magnesium has about 60 per cent of the weight of aluminum. It sold, in 1915, for $5.00 per pound and was, until a few years ago, a structural curiosity. Today, measured by volume, magnesium at 22 cents a pound is cheaper than aluminum selling at 15 cents a pound. On the average, about a half ton of it is going into every fighting plane. After the war, the nation's capacity for producing this lightest of all structural metals will be more than double the aluminum output in 1939. Published data gave the capacity of the old plant of the Dow Chemical Company at Freeport as 125,000 pounds per day, using a flood of 25,000 gallons per minute of sea water. The plant has been enlarged until the original production amounts to only a fraction of the present output. Just try to visualize two hundred tons per day of magnesium ingots obtained from sea water in which the concentration of the magnesium amounts to only around 1100 parts per million. A computation of interest is that a cubic mile of seawater carries about 10 billion pounds of magnesium—enough to run our 1943 war effort and similar ones for ten years. There, in the sea, is an inexhaustible supply of industrial material.

Magnesium is seldom used alone. Add a little aluminum and it will gain sixfold in hardness and strength. Such a commercial alloy is the exceptionally strong Dowmetal which carries about 8 per cent aluminum with a little zinc and manganese. It will be of interest to know that the war plan calls for one billion pounds of magnesium in 1943.

But iron, composing about 5 per cent of the earth's crust,

is the most useful metal. More material has been taken out of the Mesabi Iron Range than was moved in the digging of the Panama Canal. And yet there is sufficient ore to last for hundreds of years. In the case of iron, the first industrial development came with the discovery that ordinary iron could be turned into strong versatile steel through the use of carbon. Even the ancient sword-makers, who pounded out the famed blades of Damascus, knew the magical power of carbon and the correlated methods of heat treatment. Nitrogen compounds, taken from interesting sources, were used in the quenching bath. Today tank armor is "nitrated" in hot ammonia gas, and the surface is thus "case-hardened."

Steel is challenging the light metals. Low alloy steels and new modifications of the higher alloy steels, fresh from the laboratory, are bidding for expanding uses. These new alloys are three times the weight of aluminum and almost five times the weight of magnesium, but their tensile strength approximates 190,000 pounds per square inch. This advantage permits weight to be shed by reducing bulk and eliminating needless supports. The alloys are less subject to corrosion than plain steel. Putting wings on freight cars is just about what American industry is now doing—building air freighters of tremendous proportions to carry carloads of supplies to our nation's forces in the far corners of the world. Many months ago, plans were put into execution for the construction of giant all-stainless steel cargo planes—planes that would have the strength and stamina to withstand the vibrations and stresses encountered under severe flying conditions.

Precise knowledge of exactly what happens in steel formation has made possible a great variety of alloy steels with definite characteristics. Chromium, the element which imparts precious color to rubies, imparts something more precious to steel. It gives steel incredible hardness and re-

sistance to heat and corrosion. It makes steel strong, yet ductile and shock-resistant. Chromium is the key that has opened, and is still opening, great new fields of application for steel. Without chromium the whole wonderful series of stainless steels would not have been possible. From tarnish-free tableware to corrosion-resistant chemical equipment; from strong, light-weight truck bodies to streamlined trains and airplanes; from heat-defiant boiler tubes to high-temperature steam turbines, chromium has made possible a steel with desired properties of the noble metals. But the stainless steels are only one great contribution of chromium. This element has also helped to provide long-wearing engine valves, strong, tough gears, tools, ball-bearings, shafts, springs, and hundreds of other improved articles. When engineers, about fifty years ago, produced chrome-steel projectiles that easily pierced the best armor plate of the day, all the warships became obsolete overnight. The answer was, of course, armor plate of chrome-nickel steel. Some years ago we were practically dependent upon outside sources for chromium. At that time our relatively low-grade ores made it impossible for domestic producers to compete with foreign suppliers who had the advantage of richer deposits. Now concentration methods have been devised which make this ore available.

What nickel has to contribute to the industrial field is not only corrosion resistance but also physical and mechanical properties which give the metal, particularly in alloy form, definite structural importance. To a considerable extent the participation of nickel is through nichrome alloys and monel-metal, the 32-68 nickel-copper alloy which now is produced with the strength of steel.

Tungsten is another strategic metal. Since sheelite glows with a fluorescent light in the rays of an ultraviolet lamp,

prospectors hunt the tungsten at night. The richest strike yet made is in central Idaho where men, hunting for antimony, stumbled upon a very high-grade deposit of tungsten ore. To a modern industrial country, at war, there would be few catastrophes to compare with a real shortage of tungsten. It gives strength to steels and armor-piercing projectiles. It has that sterling property of getting hot without losing its temper. Tungsten carbide tools cut at speeds so great that the edge is blue-hot from the fierceness of the friction. Oil-field drilling bits are "faced" with tungsten carbide. They will drill through solid quartz.

Ranking high as a toughener of steels is molybdenum, "Moly" for short. Alloyed with steels it takes out the creep, which is the tendency of metal to stretch under strain. Of major importance is the discovery that molybdenum can be substituted for much of the tungsten in making high-speed steels. In molybdenum supplies we are indeed fortunate for this country produces more than 90 per cent of the world's requirements.

In brasses, bronzes, and innumerable alloys, copper is vitally needed for cartridge cases, bullet jackets, propellers of ships, electrical equipment, etc. Modern concentration methods have made it practicable to extract the small percentage of copper even from old waste dumps. The water, flowing from the mines, is made to yield copper—6 million pounds per year—through the utilization of your old iron cans and other iron scrap over which the water is caused to flow. The copper is replaced by the iron, forms heavy sludges, and is recovered. Less than 2 per cent of beryllium, if alloyed with copper, will make that metal so hard that it will cut steel. Used in springs and diaphragms of delicate instruments, these alloys stick to their job under fiercely corrosive conditions.

Certain finite properties in steels are gained by the addition of the alloying elements. The effects of some have been discussed. Vanadium imparts toughness to steel; selenium gives free-cutting characteristics; nitrogen leads to grain refinement; thorium, titanium and columbian inhibit carbon precipitation; sulphur gives better machining properties and zirconium is added to hold the sulphur.

Mercury, as fulminate in shells, touches off the thunder of high explosives and the fury of incendiaries. It is used in the anti-fouling paints to keep barnacles off of ships; in fluorescent lighting; and for many other purposes. One General Electric mercury boiler, supplying mercury vapor to drive a 20,000 kilowatt generator, carries 270,000 pounds of mercury in its system. Sodium metal is added to the mercury to give better heat transfer, and zirconium is added to retard the solution of the boiler iron by the mercury. It should be interesting to note that the mercury-vapor condensers are really steam boilers, operating on a lower temperature plane.

Already concentration of low-grade ores has been mentioned. One ingenious process, flotation, has added many so-called "worthless deposits" to our natural supplies. Flotation is a process whereby the grains of one or more minerals, or chemical compounds, in a pulp or slurry, are selectively caused to rise to the surface by the action of bubbles of air. The grains are caught in a froth, formed upon the surface of the liquid, and are removed with the froth, while the grains which do not rise remain in the slurry and are drawn off at the bottom. Chemical collectors, frothers, depressers, and deflocculating agents are added to increase the efficiency of the separation.

In the Minnesota district a mixture of oleic acid with pine oil, modified by sodium silicate with sodium carbonate as a protector, suffices to give excellent concentration of man-

ganese ore. The flotation of phosphates is, by far, the greatest application of the flotation process to non-metallics. In Florida 11,000 tons per day are recovered from deposits at one time considered worthless. From the standpoint of chemical engineering a novel adaptation of flotation has come in the separation of potassium chloride from sodium chloride. The crystals are separated from each other in a saturated brine made up from the crude mixed salts as they occur in natural saline lakes.

In the field of sanitary engineering appears the problem of supplying safe and relatively soft water which will be used in the municipality for home consumption as well as for the industry. Good water for drinking purposes has doubtless been appreciated by the human race from time immemorial. Among primitive peoples the question of water supply was never of passing importance, except in arid regions. Recent archeological explorations in India have shown that five thousand years ago these people were living in well-built cities provided with well-constructed water conduits covered with marble slabs. The ancient water tanks in Arabia may have been built as early as 600 B.C. The infiltration galleries for collecting ground water at Athens were probably constructed two thousand years ago. Probably no more elaborate system of public water supply was provided for any ancient city than that of Rome. Three groups of springs in the volcanic plain on the left bank of the Tiber supplied the water to be conveyed by aqueducts to the city.

The requirements for municipal water supplies are that there should be no disease organisms present, that the water should be clear, colorless, and odorless; that it should be reasonably soft and non-corrosive; that it should be free from objectionable gases and minerals; and that it should be plentiful and cheap.

A river is often the source of supply of raw water. At the water-treatment plant coagulents are added and the water passed into large settling basins. The water is then efficiently aerated, oftentimes by sprays and waterfalls of architectural splendor, in order to eliminate any hydrogen sulphide present or to oxidize the iron and manganese. Filtration removes most of the suspended materials present and, at the same time, a large per cent of the bacteria. If odors and tastes persist, activated carbon is added before the filters. If the water is too hard it may be necessary to soften it to some desired degree through the use of lime-soda chemical treatment. The prevention of excessive scale formation from hard or unstabilized water has been one of the most stubborn problems for the water plant operator to solve. By recarbonating the water following the softeners, he could prevent after-precipitation more or less completely; but if he were successful in stopping all precipitation he would very likely be plagued by red water. "Threshold Treatment" offers a new method of control. This consists of adding a very small quantity of hexametaphosphate. When two parts per million, or even less in some cases, are added to the water, all precipitation of calcium carbonate is prevented. The economic advantage of the threshold treatment is the relatively high alkalinity which may be maintained, thus inhibiting corrosion.

Although softening and filtering remove a very large per cent of bacteria present in the water, yet the water is not safe. The remaining bacteria must be killed. The practical development of chemical disinfection has occurred during the last twenty years and by far the most commonly used disinfectant is chlorine. The chlorine attacks the bacteria, causing their elimination. There are indications that there are direct chemical combinations with some forms of bacteria. After such a chemical reaction there would be a com-

pound which might be called, "Bacterium Chloride"—BCl —a chemical compound and no longer a bacterium. Some two to five pounds of chlorine are added per million gallons. An excess is added to maintain a residual chlorine content of around 0.2 part per million in order to maintain sterile conditions. By adding ammonia along with the chlorine the destruction of bacteria may be made just as certain but much less rapid. This means a greater penetration down the mains and protection even to the very end of the lines. This "chloramine" treatment was started in Houston in 1933.

We are sending our soldiers, sailors, marines, and aviators away from the safest drinking water in the world. Swamp water of the South Pacific islands, polluted streams of Europe, drainage ditches of Northern Africa—all may be endured by the natives, but they are not good enough for our men. Even during peace times travelers tell us that wines and boiled beverages are the only safe liquids that can be used to satisfy thirst when in some of these countries. There may be some difference of opinion as to whether this may or may not have been serious, but enormous amounts of good water must be furnished to our fighting men. The Army and Navy health engineers have redoubled their efforts to safeguard every drop of water which our expeditionary forces drink. As the armed forces can transport only an infinitesimal amount of the water they use, modern purification units must be on, or near, the battle lines. Chemicals are, as usual, in there battling not only to make water safe from harmful bacteria, but clear, colorless, tasteless, and odorless. Chlorine and aluminum sulphate are two of the principal chemicals employed in these light portable water-treating units.

An Army Quartermaster Corps sends out mobile laundries with our troops to all parts of the world. Each of these laundries has to keep some 15,000 soldiers' clothes clean, no

matter what part of the world it is in. And at some of the places they say that the water "is so hard that it bounces." New detergents, containing soaps which do not give insoluble precipitates with hard water, have been developed. These soaps produce a perfect lather no matter how hard the water may happen to be.

Even though the excess hardness has been removed by the municipal water-treating plant, the industrial plants, especially those in which scale may be formed due to concentration or heating, must have even softer water. For the past fifteen years the trend has been to higher steam pressures in commercial boilers. This is advisable in order to improve the plant cycle efficiency. The high pressures of former years, like 500 pounds per square inch, are giving way to pressures of 1200 or more. At high rates of heat absorption, even a scale 0.01 inch thick may cause failure due to burned-out tubes. When solutions which contain salts whose solubilities increase with an increase in temperature are concentrated beyond their saturation value, these substances deposit as sludge. If their solubilities decrease they form scale. The formation of scale occurs *in situ*, that is to say, these constituents deposit directly upon the heat-transfer surface as scale. Sludges remain in suspension and are constantly removed from the boilers by the blow-down.

At low pressures sodium carbonate may economically be added to the feed water in order to cause precipitation as sludge, of calcium carbonate, not of the chief scale-former, which is calcium sulphate. At higher pressures with associated higher temperatures, phosphates are added. They do not decompose and yet, as in the case of the carbonates, they form precipitates whose solubilities increase with temperature; and consequently they form sludge—not scale.

For the successful operation of a boiler it is just as im-

portant to protect the boiler metal from corrosion as it is to prevent the formation of scale. The mechanical engineer looks at the boiler as a perfectly solid, stable piece of equipment. The chemist considers it as something subject to continuous slow reaction between the water and the steel, the rate of the reaction being fundamentally affected by the composition of the water and materially increased by higher temperatures. The entire region of chemical protection lies on the alkaline side—in a comparatively narrow range at high temperatures. Therefore one of the essentials for protecting the boiler metal from corrosion is that the water must be maintained in this specific alkalinity range. Since the corrosion rate is proportional to the oxygen content, the oxygen must be completely removed. This can be done very effectively by mechanical deaeration followed by chemical treatment. Sodium sulphite is maintained in the boiler and serves as the vigilant policeman. It is kept ever-present in order to eliminate at once any oxygen which might slip into the system. The deterioration of boiler metal, characterized by cracking of plates and rivets along submerged riveted seams, is referred to as caustic embrittlement. This type of failure is caused by simultaneous chemical action and stress. The disastrous effect of soluble silica in alkaline solution has been conclusively demonstrated and seems to be the principal cause of such failure. Its nearly complete removal can be attained through the use of hydrous magnesium oxides. Many of the operators of boilers in high-pressure ranges regard one-piece forged or welded drums as an adequate guarantee against serious trouble caused by silica.

Many industries use distilled water as make-up for their boilers. Due to condenser leakage and the addition of chemicals for corrosion control, treatment is still necessary. Quite generally lime-soda softened water is most economical but

some waters lend themselves to softening more cheaply through the use of exchange zeolites.

By the action of hard waters on certain complex silicates, both natural and synthetic, an exchange of the calcium and magnesium for the sodium of the zeolite may be brought about. These zeolites, when exhausted, are revivified by passing a strong solution of common salt through them. After thorough washing, the cycle may be repeated. The zeolites were used originally as sodium zeolites, and since calcium and magnesium are basic, the term "base exchange material" was often applied. Research has now given us a carbonaceous zeolite, "Zeo-Karb," which is free of dangerous silica. When regenerated with sodium chloride it functions as the early zeolites. When regenerated with dilute acid, not only the calcium and magnesium, but also the sodium, may be removed. Used in this manner we have a "Zeo-Karb H" unit.

With the advent of this zeolite it became possible to replace all metallic ions with hydrogen ions, leaving only the corresponding acids in solution. Now it is obvious that if the free acids could be absorbed by some insoluble substance which could be regenerated and operated indefinitely in repeated cycles it would be possible to remove the soluble salts entirely. Such exchangers have now been developed which, in some respects, even excel the earlier cation exchangers. Typical of these exchangers is the aliphatic-amine resin, called "De-acidite." Now we have a two-step commercial unit: the first removes all the metallic components and the second extracts the acids. Deaeration removes practically all of the carbon dioxide and the effluent from the process analyzes as H_2O—nearly as free from soluble materials as if it had been distilled.

Other applications of these exchangers might be the com-

mercial removal of magnesium from sea water, the demineralizing of sugar solutions at various stages in refining, the removal of salts from many impure solutions or as a unit accessory in life-rafts for the purpose of making drinkable water from sea water.

After the water is used in the city it is sent into the sewers which convey it to the sewage disposal plant. At many such plants the sewage is aerated in large open basins so that aerobic bacteria can thoroughly digest and decompose the organic matter. Coagulents are added after mechanical concentration of the sludges; the solids are filtered out, dried, and made into balanced fertilizers. The clear, sterile, effluent water may then be returned to the river from whence it came.

Today the petroleum industry has changed from almost a non-technical industry to a very technical one. There must be a highly trained exploration and production staff, a carefully trained research and development department, a technically trained control laboratory, an engineering and refining staff, and finally, a co-ordination and sales department. Petroleum is a chemist's and chemical engineer's business. Chemical control follows the oil from its original formation to its final usage.

Soil and gas analyses indicate presence of petroleum formations. Chemical control of drilling muds insures most efficient drilling conditions. Hydrochloric acid, inhibited with amines to protect the drilling equipment from attack, is used to open up limestone formations. Emulsions must be broken to lower water content to the point where the oil can be pumped into the oil lines. Casinghead gasoline recovery plants must be designed, installed, and operated under absolute control. And finally, in the refinery, ultimate control is chemical in nature whether it be in the straight run or cracking unit, in

the acid-treating or dewaxing plant, or in the treatment of the boiler or cooling water.

Some years ago it was thought that the ultimate in motor fuel would be reached by the creation of a gasoline equivalent in power and anti-knock qualities to those of pure iso-octane. So superior was iso-octane in these respects that it was arbitrarily given the octane rating of 100, which became the standard in evaluating all gasolines. Extraordinary strides have been made in the fabrication of airplane engines, propellers, and bodies. The advances in design and construction of the engines have been made possible, to a large degree, by the oil industry in producing the 100-, and higher, octane gasoline and all the necessary lubricants. Increased manifold pressure increases explosion pressure and requires a higher octane fuel in order to avoid detonation. The use of superchargers, with high-octane fuel, increases the speed, cruising ranges, and ceilings of the planes. The use of 100-octane aviation fuel will give our aircraft a definite advantage over aircraft of our enemies and may, in effect, be one of the deciding factors of the war. The octane ratings of aviation gasoline which has been collected from captured and shot-down German planes average around 87. It has been reported that the German invasion of England in 1940 was stopped by the R.A.F. because the English fighting planes were powered with 100-octane fuel.

Tetraethyllead, the product of Midgley's researches, broke down one of the barriers that was blocking the road to automotive progress—the barrier of "knock." Added to gasoline it increased the power and performance of many million automobiles. Although tetraethyllead has played an extremely important part in increasing the efficiency of gasoline engines, it will probably lose its importance due to the high-octane gasolines which chemical technology is rapidly providing.

Military airplanes in 1928 used gasoline of about 60 octane rating. In 1931 the standard Army aviation gasoline was 87-octane and airplane engines were developed to utilize this quality fuel which gave a 33 per cent increase in power per unit weight compared to 60-octane gasoline. Engines, designed for using 100-octane gasoline, yield 15 to 30 per cent greater output while take-off distance is reduced 20 per cent and climbing speed increases 40 per cent. Leadership in aviation octane gasoline rests in the United States. Mr. Bruce K. Brown, Assistant Deputy Coordinator for War, said in September: "It has become quite evident that the needs of the United Nations for 100-octane gasoline will eventually exceed the productive capacity of all aviation gasoline plants now built, building, or authorized." Such reasoning undoubtedly led to the curtailment of the synthetic rubber program.

Cracking, in the petroleum industry, may be defined as the breaking down of the hydrocarbon molecules into smaller ones with attendant polymerization and other side reactions. When cracking by heat was first recognized, its only commercial significance was as a possibility for producing more kerosene from crude oil. The process was stimulated by the advent of the automobile and the airplane. Cracking, in the beginning, was a thermal reaction taking place in liquid phase. The stills became a combination of pipe still, pressure reaction chamber, and fractionating tower. The Burton, Cross, Dubbs, Holmes-Manley, tube and tank, and other processes were modifications differing in engineering design. The science of cracking is distinctly an American development and its commercial application an American achievement.

Later research showed that high temperature favored the production of better octane fuels. Cracking was developed

to take place at high temperature in the vapor phase. The vapor phase processes, like the deFlorez and the Gyro, produced a higher octane product but gave a mixture rich in unsaturated hydrocarbons and thus suffered in stability. The problem confronting the chemist a decade ago was to convert the straight-chain hydrocarbons, which have low octane numbers, to the so-called side-chain hydrocarbons which have much higher octane numbers. Most of the development in recent years has been along the line of catalytic cracking. By means of suitable catalysts the desired reactions have been made to take place at lower temperature and the effect of the undesirable high temperature reactions has been minimized.

Gasoline may be made from petroleum gases by polymerizing, which is the combining of two or more simple hydrocarbon molecules into a more complex one. Thus, for example, when two molecules of the unsaturated hydrocarbon butylene combine they form dibutylene which is still an olefin, but is now a liquid instead of a gas. The catalyst, phosphoric acid, polymerizes olefins in cracked gases to motor fuel of high octane rating. This same catalyst is used for the production of 100-octane aviation gasoline by selectively polymerizing butylene to iso-octene and hydrogenating the latter to iso-octane. This simple polymerization process made a revolutionary change in the oil industry. This process is conserving crude oil at the rate of many million barrels per year, and in addition is producing a motor fuel superior to that derived directly from crude oil. The interesting point is that these gasolines are being obtained from refinery gases which were once burned only as fuel.

Another process, called "Alkylation," refers to the uniting of an olefin and an iso-paraffin in the presence of sulphuric or hydrofluoric acid catalysts. What makes these processes so

important is that, in every case, these molecules unite in side-chain arrangements and the resulting synthetic gasoline has an octane number approaching 100. Thus a high-quality gasoline is developed and a use found for the 300 billion cubic feet of practically waste gases formed yearly by the cracking process.

Isomerization is the conversion of straight-chain to branched-chain molecules. The need for isobutane, in alkylation, has emphasized this isomerization of normal butane. The new Isomate process isomerizes pentane and hexane to form a product to be used directly in gasoline. Hydrochloric acid and aluminum chloride are used as catalysts.

In the hydroforming unit the catalyst converts low octane naphtha into high octane aromatic gasoline. This process involves the circulation of hydrogen in the admixture passing over the granular catalyst. A yield of as high as 20 per cent toluene is obtainable. On the basis of 7500 barrels of naphtha feed per day, a toluene production of five million gallons per year, would be possible. The enormous production of toluene, when made into TNT, Tri-nitro-toluene, will provide very effective April showers for Germany . . . showers of four- and eight-ton "Block Busters."

Catalytic cracking processes may be broadly classified according to the physical state of both the catalyst and the reacting hydrocarbons in the reaction zone. These hydrocarbons may be reacted in either the liquid or vapor phase, whereas the material acting as a catalyst may be solid, liquid, or vapor. In the present commercially important processes for catalytic cracking, the Houdry, Fluid Flow, and T.C.C. (Thermofor Catalytic Cracking), the hydrocarbons are substantially vaporized and cracked in the presence of solid catalysts.

Many types of catalysts have been developed for use in

these three processes, but at the present time contact—or adsorptive—type materials, comprising chiefly silica-alumina composition, made by synthesis or by the chemical treating of natural clays, are used almost exclusively for this purpose. Cracking processes, employing the solid-type catalysts, may be divided further into two basic types according to the method of applying the catalyst. One system appears in which the catalyst mass remains static in the reaction zone and the vapors pass over the fixed catalyst bed. The Houdry units exemplify this type. The other is one in which the catalyst moves continuously through the reaction zone. The Fluid Flow and TCC belong to this class. The differences between the TCC, Houdry, and Fluid Flow processes lie chiefly in the physical methods employed in handling the catalyst, in its size, in contacting the oil, and in regenerating the catalyst.

The first Houdry units were placed in operation in 1936. In this system a number of catalyst units, alternately operated as a catalyst chamber and then being regenerated, serves to maintain a continuous flow through the complete unit. In this system the catalyst remains fixed in its case, serves as a catalyst, is regenerated, and used again.

The TCC process, licensed by Houdry, derives its name from the Thermofor, spiral-finned, type of clay-burning kiln which is employed as the catalyst regenerating unit. In the TCC the catalyst is in the form of granular pellets of from 4 to 60 mesh size. In this form the catalyst mass flows freely through the equipment. There are separate reactor and regenerating systems through which the catalyst is continuously circulated countercurrent to the oil vapors. This system is recognized as a short, low-cost way to more source materials for 100-octane gasoline, butadiene, and toluene.

Another improvement in catalytic cracking is the Fluid-

Flow process in operation by the Standard Oil Company of New Jersey. In this process, instead of passing oil vapors through a catalytic bed, the process uses a powdered catalyst so fine that it acts like a liquid—is carried along by the very vapors it cracks. The catalyst ranges from 30 mesh down to a few microns in size. As a powder, the catalyst exposes an enormous amount of surface. In the reaction chamber the oil is quickly cracked and the vapors, gases, and carbon-coated catalyst move on, the catalyst is separated out, regenerated, and thus made ready to use again. Meanwhile the cracked oil goes into conventional fractionating towers from which emerge base stock for making 100-octane gasoline, special octane blending agents, and other hydrocarbons which are the raw materials for alcohols and butadiene.

Researches in the oil industry are tending toward the production of single hydrocarbons as gasoline in order that the combustion conditions of the modern motor may be controlled to a high degree of exactness. With the mixture of hydrocarbons now in general use as gasoline, precision control is not possible. The motor fuel of the future will probably be a blend of a few hydrocarbons, with the proper volatility to suit prevailing climatic conditions, with an octane rating of around 100, and accurately adjusted to give all the other required properties. Looking upon the situation that is indicated after the war, the petroleum chemist sees all existing motors as out of date. Weights of post-war cars may be half of what they are now. The power output per cubic inch of piston displacement may double or even treble present values. The fuels, which will also yield more miles per gallon, will thus be "tailor made."

Whether in the bitter cold of the Arctic or in the uniform fifty-below-zero temperature of the stratosphere, machines of war have a job to do. Their motors and gears require

lubricants that flow, that lubricate thoroughly at all times. Chemicals of the sulphonate type are blended with the oil or grease at the refinery. Such lubricants permit oil to reach moving parts instantly, and gear lubricants are always efficient even under the most severe conditions. These materials, the real composition of which is kept secret, permit the oils to have only a small change in viscosity with enormous changes of temperature. The lack of such a product may well be one of the contributing reasons why Germany's power is much weaker in the severe winter cold of Russia.

War has created new and unforeseen shortages that must and will be met. Diplomatic and military defeats have created a drastic shortage of rubber. Few people can realize the immensity of the task that faces the rubber industry in changing over from the use of natural rubber to synthetic raw materials. Entirely new manufacturing and compounding techniques are required. For not only is there a fundamental difference in the various synthetic raw materials, but in their processing characteristics and in the properties of the finished goods as well.

Most people think of synthetic rubber in terms of tires, tubes, and similar finished products. But to the rubber goods manufacturer it is simply a new raw material out of which he must fashion such products. For the various chemical compounds we call synthetic rubber are very different from the stuff that comes from the trees. In fact, they have very little in common with natural rubber except resilience and elasticity—the ability to stretch and bounce. This, of course, does not mean that they are inferior. On the contrary, some are decidedly superior in many respects. But it does mean that the manufacturer must develop new compounding materials and new processing techniques. The manufacture of synthetic rubber can be as temperamental as the compound

itself is complex. And time is so important—for millions of tons of chemical rubber are needed to help bring the war to a victorious conclusion. Reserves of raw rubber amounted to about 700,000 tons at the beginning of 1942 and synthetic rubber capacity was scheduled at the rate of 40,000 tons per year. Contrast with this the first synthetic rubber program which called for 886,000 tons in one year.

When Bernard Baruch and his committee estimated last summer that the country must have about one million long tons of synthetic rubber a year to get by, that sounded to the public like the final word. But, not long ago, the United States learned that it was going to have to get along with a lot less. From Economic Stabilizer Jimmy Byrnes came an order to blunt Bill Jeffers: as Rubber Director, he could have top priorities on only enough key equipment to produce 425,000 tons of synthetic rubber this year. The vital materials for the original program could only come from still more desperately urgent war needs—building of naval escort vessels and manufacture of high-octane aviation gasoline.

In general, the synthetic rubber is at least equivalent to the natural. Synthetic rubber is superior in gasoline, oil, and chemical resistance; is more stable to light and air; and has greater wearing properties. Some trucks using synthetic rubber tires have gone over 35,000 miles. One may feel certain that as good as synthetic rubber is today, it will be far surpassed by that yet to come. Producers of natural rubber depend upon the life cycle of the rubber trees, and climatic and soil conditions—while the chemically-produced rubber will ultimately have the exact properties for which its structure and use were designed.

There are some six varieties of synthetic rubber which exist in the form of many types and grades. Well over a thousand different synthetic rubbers are known and no one

of them is a chemical duplicate of natural crude rubber. Of these six varieties, four of them, namely, Thiokol, Neoprene, Koroseal, and Butyl, originated in this country.

The several types of synthetic rubber being marketed under the name "Thiokol" are the result of research initiated in early 1920. It is produced by the Thiokol Corporation from the non-critical materials, ethylene, sulphur, and salt. The basic chemical reaction involved is that between sodium polysulphide and ethylene dichloride. Thiokol is proving to be a very satisfactory tire-tread material and may be the answer to required retreads.

About ten years ago du Pont was actively engaged in a search for a method of making butadiene rubber from acetylene. In the course of the research the acetylene was treated with hydrochloric acid giving a rubbery material. The resultant "Neoprene" is now produced by the polymerization of the addition-product of vinyl acetylene and hydrogen chloride. This new material found its way into literally thousands of different products where it proved of inestimable value. It was used despite the ready availability of natural rubber and despite a substantial difference in price. Since early in 1941 it has been so much in demand that it was necessary to place it under mandatory priority control. Engineers use it in the form of molded goods, as diaphragms, belting, lining in oil hose, in the construction of barrage balloons, and for heavy-duty tires.

Goodrich's Koroseal is produced by the polymerization of vinyl chloride with itself or with other compounds like vinyl acetate. Its distinction is resistance to chemical attack. But it lacks elasticity. It is used by the ton for cable covering on battleships because it will not burn.

Another type of rubber is based upon the dehydrogenation of isobutane, obtained from natural or cracked gases, to

isobutylene. This is polymerized with some butadiene or isoprene resulting in a product called Butyl rubber. Butyl rubber is not as good a synthetic rubber for tire use as the Buna-S. The last type, and the one looked to at present as the most satisfactory, is "Buna" rubber. The two best known Buna compounds are Buna-N and Buna-S. Buna-N is the result of building up butadiene and acrylonitrile; and Buna-S is butadiene with styrene. Compared to natural rubber, Buna-S is poorer in tear resistance, heat build-up, and flexing, but superior in aging and resistance to abrasive wear.

Since styrene is now readily made from coal and oil, the chief problem of supply is to make the butadiene. The chemist has a choice of processes—to make butadiene from petroleum products, from starch (grain or potato), or from acetylene. Russia elects potato starch as her basic raw material, converting it into alcohol and by a catalytic process, converting the alcohol into butadiene. Our chemists have greatly improved the Russian process, and there was powerful pressure from farm interests to make this the official method. Claims of quicker production, lower costs, and the use of less critical metals in construction, filled the air with controversy. However, the oil companies began their work earlier, and have contracts. On January 30th there was an announcement that the new Standard Oil Company plant in Louisiana had started production of butadiene with an estimated output of 9,000 tons per year. Many other plants have been producing butadiene in large quantities.

Certain special uses of synthetic rubber are new. When you read of a badly shot-up American plane returning safely to its base, the chances are that Butyl rubber deserves a share of the credit. That is because all American battle planes being built today have gasoline tanks protected by a bullet-sealing lining of soft gum insulated by a gasoline-resistant

synthetic rubber. So swift and efficient is the self-sealing action of these linings that they lose only a few drops of gasoline when pierced by bullets that leave jagged, fist-big holes in ordinary metal tanks.

Government and transportation officials recently inspected a special test car of the Pennsylvania Railroad which was fitted with synthetic rubber bags containing oil. One of these bags, when inflated, will hold about 13,000 gallons of liquid. The development of these bags may convert freight cars into rolling tankers, cargo planes into flying gas stations, thus providing some relief to the present petroleum transportation problem. Small filling stations that float on the sea like buoys have been developed by Navy men for the quick refueling of submarine-hunting seaplanes and other aircraft. The "filling stations," fuel-filled balloons, are lowered into the sea where they float.

Medium sized tanks require around 500 pounds of rubber, a pontoon for a bridge 1,000 pounds, each gas-mask uses about a pound, and a battleship uses up to 150,000 pounds.

In its growth the Plastics industry has followed two paths of endeavor: that toward the improvement and creation of new thermoplastic materials, as typified by Hyatt's celluloid; and that toward the improvement and creation of thermo-setting materials as typified by Baekeland's plastics. Hyatt, in 1868, discovered that nitrocellulose, combined with camphor, gave celluloid which was a desirable substitute for ivory. By the careful study of the illusive chemical reactions involved, Baekeland succeeded in finding methods for controlling the action of phenol and formaldehyde. He produced a beautiful, hard, transparent material that looked very much like natural amber.

Search for an ester of cellulose, more stable and less flammable than the nitrate, led to the development of the

acetate. Cellulose acetate is made so clear that it is widely used in the manufacture of shatterproof glass. Research led to a new group, the vinyl plastics. First were the esters of vinyl alcohol—vinyl acetate and vinyl chloride. The casein plastics—the base material being milk—appeared over twenty years ago.

Among the thermosetting plastics are urea formaldehyde condensation products like Beetleware; others of melamine formaldehyde like Melamac and some like Bakelite and casein. Among the thermoplastic types are Pliofilm, which is so freely used as a protective covering in sheet form and is made by adding hydrochloric acid to the unsaturated linkage in rubber; Neoprene and Koroseal which have already been discussed; the cellulose acetate as Celanese; the safety film, used in projection lanterns, called Lumarith; the methacrylate resins used in the aviation industry as Plexiglas and Lucite; Rayon and Cellophane, which are merely reprecipitated cellulose; and finally, Nylon.

In 1928 chemical research developed a material with far-reaching implications, both in the scientific and commercial worlds. This material was called Nylon—the first truly synthetic fiber. The so-called "66" polymer, made by the reaction between hexamethylenediamine and adipic acid, was developed. In 1938 du Pont announced the development of this Nylon from which could be spun textile fibers surpassing, in strength and elasticity, any previously known textile fiber either natural or synthetic. It is remarkable that Nylon can be made from such abundant raw materials as coal, air, and water, and that it can be fashioned into material as fine as a spider web or as thick as a man's arm. The first commercial plant went into operation in 1940. Today the entire production facilities of du Pont's two Nylon plants are being devoted to the manufacture of products for use in connection

with the war effort. A process, to make new Nylon out of old, has been completed—thus converting ladies' used Nylon hose into parachute cloth and similar materials.

Early in the defense program the Army and Navy evolved a beautiful pair of ground glass goggles mounted in precisely machined metal frames. Even before the approved design went into production it was clear that they could not be provided either in time or in required quantity. Here a crisis was averted by the Polaroid Corporation, which had developed a new process for finishing the surface of cellulose acetate sheets which gave the plastic the optical qualities of fine ground and polished glass. The result was the interchangeable plastic lens in a snug-fitting frame of molded synthetic rubber. For protection against wind, a clear, "Wind-foil" lens is worn. When the sun grows bright and glare becomes bothersome, the Polaroid "Glare-foil" lens is snapped into place.

A very important use of Plexiglas is for the production of hoods for pilots and gun turrets on airplanes where high visibility is so essential.

Laminated safety glass is a result of much research. Ceramic chemists worked out suitable formulae for the glass. Chemists developed the plastics which are being used in the interlayer, evolved the plasticizers that render this interlayer flexible, and invented compositions to make the plastics adhere to the glass. The plastic interlayer employed in the original "Triplex" was cellulose nitrate. This material decomposed under the influence of the shorter wave-length portion of solar radiation, turned brown, and lost its adhesion properties. Cellulose acetate, which is now used, is not appreciably affected by sunlight and does not decompose. When broken, the glass fragments remain anchored to the plastic and also yield to applied force. A new laminated glass,

made with acrylate resin, bulges under impact and thus absorbs the kinetic energy of the blow. To develop bird-proof windshields for airplanes, Westinghouse shoots previously electrocuted poultry from a 20-foot air gun at a pane of glass. One type of panel developed has tempered glass on the outside, an air space, then two panes of glass holding a half-inch filling of plastic. These panels protect from a 300-mile-per-hour poultry bullet.

One of the first industries in America was the manufacture of glass. In 1608, Captain John Smith established a glass factory at Jamestown, Virginia. During the following three centuries the glass industry was essentially a rule-of-thumb process. Today the glass industry has emerged from the ages of closely-guarded secret formulae and empirical processes, to a full use of the tools of modern science. The outstanding advantages of glass are its inertness, durability, transparency, and cleanliness. The Corning Glass Works has developed a glass with high heat resistance coupled with high chemical stability. This "Pyrex" glass has the lowest coefficient of expansion of any commercial glass, which makes it unequalled in its ability to withstand sudden temperature changes.

The first glass-lined steel tanks were manufactured solely for the bulk storage of malt beverages. Their advantages gradually led to their adoption by other industries, particularly chemical and food. The linings are of complex borosilicates which are fused to the steel at temperatures averaging about 1800° Fahrenheit. It is the glass-lined tank car and truck tank which has made the hauling of bulk milk practical. The thermal expansion of these enamels can be conveniently controlled by adjusting the sodium oxide and the boric acid contents, the former raising the expansion and the latter lowering it.

A special use of Pyrex is found in the construction of a telescope with a 200-inch, 20-ton reflecting mirror. For electrical insulation, glass filaments are spun and make a flameproof wire coating for use in heavy bombers. Glass fiber boards are used for heat insulation in fighting planes and in the new Arctic shelters for the Army Air Forces where the temperature falls to 65° below, with howling snowstorms. Glass foam has found use in displacing cork in life preservers and life boats. Spun glass is used as a fireproof textile. Some of the newer optical glasses use no sand at all, but depend upon the rare earth elements such as tantalum, tungsten, and lanthanum. The glass made from these materials is highly satisfactory for use in aerial photography lenses, giving more sharply defined images at higher altitudes.

The basic idea which is stimulating industrial activity is generally chemical information. The enormous industrial plant, consisting of an amazing variety of machines and equipment, is the scientific outcome of translating this knowledge into useful production. For instance, in the making of fertilizers, explosives, and other chemical compounds, nitrogen is extracted from air's inexhaustible supply. From raw sulphur is made sulphuric acid—the use of which may be taken as the index of a country's industrial activity. From common salt comes, by electrolysis, caustic, chlorine, and hydrogen. Phosphate rock is chemically altered to fertilizer and other valuable phosphorus compounds. When sufficient heat is applied, shell and clay become cement; clay is changed to brick and tiling; sand becomes glass; coal yields coke for our steel mills, ammonia for fertilizer and tar for innumerable uses. Cane and beets supply us with our rationed sugar. Wood is distilled for acetic acid, turpentine, and rosin, or is chemically disintegrated to furnish high-grade cellulose for paper, viscose, and nitro-cellulose. There are the mammoth

industrial enterprises which supply us with prepared foods, drugs, dyes, flavors, essential oils, photographic materials, and myriads of other necessary products.

Farm chemurgy is defined as putting chemistry to work for the farm. Great gains in national wealth have come largely from new inventions, new scientific discoveries, and the utilization of neglected materials. Grains are being converted into alcohols. Oathulls yield furfural. Soybean oil is used in paints, while tung and linseed oils are used in varnishes. Cornstalks and sugar-cane bagasse make insulating board. Cotton furnishes cellulose for nitro-cellulose. The cottonseed meal is used for stock feed and fertilizer. The cottonseed oil becomes a valuable feed in the form of salad oils and lard substitute. By the addition of hydrogen, it is possible to transform the oil into solid shortening. Fluffing with nitrogen inhibits oxidation and makes it stable for longer periods of time. Dextrin, made from sweet-potato starch, is used as an adhesive on postage stamps. Agripol and Noropol are synthetic rubbers made from the fatty acids of vegetable oils. Ethylene is used for the purpose of rapidly ripening fruits. The speed of growth of potatoes has been increased nearly 100 per cent when the seedlings have been treated with ethylene. Insecticides, fungicides, and disinfectants have been developed to protect the crops.

When the nation entered the first World War in 1917, there existed no organization in the Army devoted to the pursuit of chemical warfare or to protection against it. This handicap, however, was largely overcome thanks to the feverish researches of many American chemists. This new and revolutionary form of warfare became so important that it was necessary to establish a separate organization within the Army devoted to the study of chemical warfare.

The Allies did not believe that the Hague rules of warfare,

which prohibited the use of poison gases, would be wantonly broken. But in April, 1915, the Germans launched the first gas attack. The military situation had reached a stalemate and the vast stage was set. With all weather conditions correct, several thousand cylinders of chlorine gas, previously installed in the German trenches, were opened. The poisonous gas, drifting over the soldiers of two French divisions was so unexpected, so powerful in its effects, so sudden, that the men who were not overcome fled in terror and confusion. The attack was devastating in its effects. The German troops were able to penetrate, unopposed, to a depth of three miles where they entrenched. Had they pushed on, they might have been able to reach the sea, thus breaking the blockade which slowly but surely was starving Germany into submission.

From that day each warring nation mobilizes its chemists to devise offensive and defensive methods of chemical warfare. Thousands of compounds have been investigated to determine their suitability, but the requirements which chemical warfare agents must possess are so specific and rigid that not more than a score have been found to have value. Chlorine is an irritant. It causes inflammation of the respiratory organs, produces quick disability, and may cause death. Phosgene or carbonyl chloride is a colorless gas having a sweetish odor. It, too, is a lung irritant. It is much more toxic than chlorine. The next development was the use of chloropicrin, which causes nausea and made it impossible to keep the gas-mask in position. Mustard gas, or beta chlorethyl, dissolves in skin or lung tissue and produces serious burns. It is a highly effective casualty producer. Lewisite is another dangerous agent. The lacrimators, or tear gases, produce a copious flow of tears and intense eye pains. The Army chemists have developed a standard gas mask which

provides complete protection to the eyes and to the respiratory organs, against all known chemical warfare agents. Methods are being worked out for the protection of the body and suitable material for this purpose has been produced.

In the present war, chemical weapons have as yet played no important part; but smoke screens and incendiary agents are being used. Both Great Britain and Germany have made great efforts for defense against gas attacks, and doubtless both nations have the means to conduct vigorous offensive action with chemical agents. Possibly the fact that Germany is unable to keep her enemies from coming over her country accounts for her not starting chemical warfare. But it is by no means certain that chemical warfare will continue to play a negligible rôle in this conflict.

The nation will emerge from this war with enormous capacities for making plastics, synthetic fibers, nitrates, hydrocarbons, high-octane fuels, and many other raw materials on a scale that only two years ago was beyond our comprehension. In a world at war the impression is given that all forces are used solely for destruction. When the war is over, the new technology will quickly, efficiently, and effectively convert the war effort to peacetime pursuits with amazing speed. With the tremendous pressure of necessity, commercialization of processes has occurred which would have taken years under normal conditions to complete.

But now Chemical Industry is fighting for an American victory and an American peace.

A. J. HARTSOOK.